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固态/液态混合聚碳硅烷制备 SiC 纤维的关键基础研究

Preparation and Characterization of Silicon Carbide Fibers
from the Blend of Solid and Liquid Polycarbosilanes

汤 明

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Preparation and Characterization of Silicon Carbide Fibers from the Blend of Solid and Liquid Polycarbosilanes



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Doctor of Philosophy

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摘 要

为了改善高分子材料的性能,对已有高分子材料进行物理共混改性是一种经济而有效的途径,也是先驱体法制备新一代高性能 SiC 纤维的研究热点之一。

本研究首次将超支化液态聚碳硅烷(LPCS)与固态聚碳硅烷(PCS)进行物理共混改性,得到改性的 PCS 先驱体。改性后先驱体经过熔融纺丝得到原丝,原丝经氧化交联得到交联丝,最后交联丝在 1250℃氮气气氛下热解得到 SiC 纤维。本论文对上述的制备工艺中的关键基础问题进行了系统研究。

LPCS 具有与固态 PCS 相似的分子结构,相容性好,不需要采用复杂的真空冷冻技术,通过普通的物理共混方法便可以得到混合均匀的先驱体,混合过程中没有发现明显的相分离现象,固液混合先驱体的组成和分子结构基本是固态 PCS 和 LPCS 的物理叠加。

LPCS 的加入明显提高了先驱体中 Si-H 基团的含量,红外谱中 Si-H 与 Si-CH₃ 的比例从 0.91 (不含 LPCS, PCS-0) 提高到 0.98 (含有 20%LPCS, PCS-20),核磁氢谱中 Si-H 与 C-H 比例从 0.096 (PCS-0) 提高到 0.14 (PCS-20),有利于后续交联工艺。在熔融纺丝过程中,有部分 PCS 和 LPCS 发生交联反应,消耗一部分的 Si-H 基团,但先驱体中的大部分 Si-H 基团得到了保留。经过高温熔融纺丝后,LPCS 能够稳定存在于先驱体纤维中。

LPCS 的加入明显降低了先驱体的纺丝温度,从 285℃ (PCS-0) 降低到 205℃ (PCS-20)。由于 LPCS 延长了熔体的固化区间,因此显著改善了先驱体的纺丝性能,纤维的直径和分散系数明显下降,从 19.6±1.8μm (PCS-0) 降低到 15.4±0.5μm (PCS-20)。同时由于纺丝温度的降低,改善了先驱体的热稳定性。LPCS 提高了原丝的表面质量,减少纤维表面缺陷。

PCS 原丝在空气氧化交联过程主要是 Si-H 键被氧化成 Si-OH 键, Si-OH 与 Si-OH 发生缩合反应生成 Si-O-Si 交联结构的过程,此外也有 Si-CH₃ 氧化生成 Si-OH,促进交联结构的形成。在交联过程中形成的挥发物中,含有水和甲醛,从而首次从实验上证明了 SiC 纤维的先驱者 Yajima 教授所预测的氧化交联机理。

LPCS 促进氧化交联,因此可以在较低温度下实现氧化交联。在 150℃氧化温度下,纯 PCS 交联丝的凝胶含量为 0,而含有 20%LPCS 的交联丝凝胶含量达

到 80%，这不仅是因为 LPCS 中含有大量易于与氧反应的 Si-H 键，而且还因为 LPCS 分子量较小，通过共混可以均匀分布在 PCS 分子中，在交联过程中，起到了交联点的作用；

LPCS 含量 10% 以上的所有纤维经 1250℃ 热解后均能保持原状不并丝，而 LPCS 含量 5% 以下的纤维，经 150℃ 氧化交联和 1250℃ 热解后发生并丝现象。LPCS 的加入，可以提高纤维的陶瓷产率，加入 10% 以上的 LPCS，原丝只要经过 150℃ 氧化交联，其陶瓷产率均在 81% 以上，而经 150℃ 氧化交联的纯 PCS 纤维陶瓷产率只有 77.6%。

相同氧化交联温度下，固液混合 PCS 纤维中含有较多的 SiC_xO_y 无定型相，抑制了 $\beta\text{-SiC}$ 微晶的生成和长大，纤维中的无定型碳的比例高于纯 PCS 热解纤维。利用固液混合 PCS 纤维所制备的 SiC 纤维的拉伸强度 (1.76GPa) 低于由纯 PCS 纤维制备的 SiC 纤维 (2.81GPa)，这主要是由于氧含量过多以及氧在纤维径向不均匀分布的结果。在空气高温处理过程中，由 PCS 制备的陶瓷纤维拉伸强度随温度的提高逐渐降低，而由含 LPCS 先驱体制备的陶瓷纤维拉伸强度保持率在 1400℃ 之前几乎为 100%，这主要是因为含 LPCS 的纤维其表面有一层富氧层，阻止了氧进一步扩散到纤维内部使其继续氧化。

关键词：先驱体转化法；固态聚碳硅烷；超支化液态聚碳硅烷；氧化交联；SiC 纤维

Abstract

Polymer alloying is to mix different polymers to obtain the desired properties. It is widely used in industry because of its convenience, economy and adoptability. It is also one of the major interests in silicon carbide fibre production for the development of high-performance and low cost fibres.

In this work, highly branched liquid polycarbosilane (LPCS) was used as the alloying polymer to modify the properties of polycarbosilane (PCS). The resultant blend is used as the precursor for silicon carbide ceramic fibres. The blend is melt-spun into precursor fibres, oxidation-cured in hot air, and finally converted into silicon carbide fibres by pyrolysis in nitrogen. The key scientific problems encountered in the processing are comprehensively studied in this thesis.

LPCS has similar molecular structure to PCS. Therefore, they have good compatibility. A homogeneous blend can be obtained simply by mechanical mixing, making the expensive vacuum drying unnecessary. No obvious phase separation or chemical reaction is observed during the preparation. The blend is essentially a physical mixture of the two components.

The addition of LPCS into PCS increases the Si-H concentration in the precursor. On the base of the FTIR spectra, the Si-H/Si/CH₃ increases from 0.91 for PCS to 0.98 for 20% LPCS/PCS. From ¹H-NMR, the Si-H/C-H increases from 0.096 for PCS to 0.14 for 20% LPCS/PCS. The high Si-H concentration is conducive to the subsequent oxidation curing.

During melt-spinning, LPCS is partially reacted with PCS, consuming some Si-H. However, an overwhelming majority of them is preserved. In the precursor fibres, LPCS is stable during storage. LPCS reduces the spinning temperature significantly, from 285°C for PCS to 205°C for 20% LPCS/PCS. Because the LPCS prolongs the solidification of the extruded filament, the spinning ability of the precursor is markedly improved. The fibre diameter and the diameter distribution are also improved. For example, the fibre diameter decreases from 19.6±1.8μm for PCS to 15.4±0.5μm for 20% LPCS/PCS. The reduced melt spinning temperature is beneficial to the thermal stability of the precursor. The LPCS also improves the surface quality, reducing the surface defects.

The major reactions occurred during oxidation-curing are the oxidation of Si-H

bonds, forming Si-OH groups. Condensation reactions then takes place between the Si-OH groups, producing Si-O-Si linkage, which is responsible for curing. At higher curing temperature, Si-CH₃ groups are also oxidized into Si-OH, further promoting the curing process. Water and formaldehyde are the major gaseous species evolved during oxidation curing. This is the first time to experimentally confirm the proposed oxidation mechanisms by Prof Yajima.

LPCS promotes the oxidation curing because of its richness in Si-H groups. Therefore, the fibres can be rendered infusible at lower curing temperature. At 150°C, the gel fraction of the cured fibres from PCS is almost zero, while for 20% LPCS/PCS precursor fibres, it is 80%.

When LPCS is over 10% in the precursor, the fibre shape can be retained after pyrolysis at 1250°C. But when it is <5%, oxidation at >150°C is needed to produce sufficient curing. LPCS addition improves the ceramic yield to 81% for 15% LPCS/PCS from 77.6% for PCS.

For the same oxidation temperature, the LPCS-containing precursor gives the ceramic fibres with higher SiC_xO_y fraction, suppressing the growth of β-SiC crystallites. The introduction of LPCS into the precursor results in ceramic fibres with lower tensile strength (1.76GPa for 15% LPCS/PCS) in comparison with the PCS-derived ceramic fibres (2.81GPa). It stems from the non-uniform oxygen distribution because of the active nature of LPCS toward oxygen. However, the strength retention at 1400°C is almost 100% for the 15% LPCS/PCS-derived fibres, much higher than the PCS-derived ceramic fibres. The main reason is that there is an oxygen-rich surface layer in 15% LPCS/PCS-derived fibres, impeding the diffusion of oxygen into the interior of the fibre and hence slowing down further oxidation.

KEYWORDS: Polycarbosilane; Highly branched polycarbosilane; Precursor; Oxidation curing; Silicon carbide fibres

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